XXXII. Remarks on a certain Kind of Organic Matter found in Sulphureous Springs. By Charles Daubeny, M.D., F.R.S. and L.S., Professor of Chemistry in the University of Oxford.

Read June 7, 1831.

The general occurrence in certain thermal waters of a substance which, from its general aspect, as well as from certain of its chemical properties, is thought to possess a claim to be classed among animal products; the medical importance that has often been attached to its presence; and the singular theories by which its existence has been explained,—are circumstances, that combine to confer an interest on any observations calculated to throw light upon the real nature of such a phænomenon.

Hence, though the present communication may, perhaps, be regarded as little more than a confirmation of what has been already affirmed with regard to the hot springs of Aix in Savoy, by Saussure*, and the cold sulphureous ones of this country, by Dillwyn⁺,—yet the additional evidence to the same effect which I have to offer, derived from an examination of certain thermal waters in France last summer, will not be regarded as superfluous, when it is recollected that, in defiance of the statements of the above-mentioned naturalists, several crude notions and erroneous hypotheses prevail concerning this

* Vide Journal de Physique for 1790, p. 410.

+ Dillwyn's British Confervæ, p. 54.

deposit,

deposit, which have served to throw a certain air of mystery over its nature and origin.

I am therefore induced to lay before this Society a drawing*, which represents the appearances exhibited, under a microscope of Amici's construction, by an organic substance which I obtained last summer at the hot spring of Greoulx in Provence (departement des Basses Alpes). This matter was found everywhere on the pavements of the bathing-rooms, in parts exposed to the splashing of the thermal water, which, for the convenience of topical bathing, or the *douche*, is usually allowed to descend in a constant stream from an open pipe, communicating with the reservoir which receives the mineral water, and terminating just below the ceiling of the room, through which it passes in a direction nearly perpendicular.

The substance alluded to, seen by the naked eye, has a greenish tinge, and seems made up of bundles of filaments : under the microscope, however, the latter are magnified into long cylindrical tubes, almost transparent, and divided into articuli, the length and diameter of which appear nearly equal, filled with a darkish fluid, whilst the intervening spaces are nearly colourless. This appearance may, perhaps, be explained by supposing a double tube, the exterior one transparent and continuous throughout, the interior composed of articulations filled with a coloured matter, and distinct one from the other, in conformity to the general structure of *Confervæ*, as laid down by Bory de St. Vincent⁺ and others. These same filaments are sometimes so disposed with reference one to the other, as to present a stellated appearance of greater or less regularity.

In fig. 5. of the plate representing Arthrodiæ, which is given in the 2nd volume of the Dictionnaire Classique d'Histoire

- * The drawing is deposited in the Library of the Society.
- + Dict. Classique d'Hist. Nat., article "Arthrodiées."

Naturelle, may be seen figured an Oscillatoria, the filaments of which are disposed a good deal in the same manner; and Vaucher, in his work on $Conferva^*$, has depicted, under the name of Oscillatoria major, an appearance very similar in kind to the cylindrical tubes detected by the microscope in my specimen. Now this particular species of Oscillatoria is one of those found by Saussure in the hot springs of Aix near Chambery, occasioning there a deposit in the canals and cisterns of the baths, which, notwithstanding the explanation thus long ago afforded of it by the above able naturalist, continues even at the present day to give rise to much speculation and wonder.

The mineral water of Greoulx resembles in constitution that of Aix, being a hot sulphureous spring, possessing a temperature of 31° Reaumur, and containing, according to the Report published by the proprietor of the baths, the following saline ingredients in the pint.

Common salt		•	12.25 grains	š .
Muriate of magnes	sia		1.75	
Sulphate of lime			1.66	
Carbonate of lime			3.00	
Total			18.66	

The quantity of organic matter present in the water of Greoulx is estimated in the above document at no less than 6.66 grains to the pint; but the greater part of this quantity must have been merely suspended in the water; for a portion of it, which I collected on the spot, being evaporated to dryness, gave but very feeble indications of ammonia, or of any animal or vegetable matter whatsoever.

A substance altogether similar to that from Greoulx was found

* Geneva, 1803.

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in the analogous thermal spring of Digne in the same department. I met with it, as at the former locality, wherever the water was allowed to drop upon the floor of the bath.

When examined under Amici's microscope, it presented a fibrous structure, the filaments being so interlaced as to form a kind of network. These filaments by a stronger magnifying power exhibited the same appearance of tubes with granulations, as those did from the former locality.

Among the hot springs which are so abundant in the Pyrenees, I collected several samples of this same organic matter, and remarked, that when the spring from which it had been obtained was impregnated with sulphuretted hydrogen, the appearances approached those already described.

Thus, at Arles in the departement des Pyrenées Orientales, south of Perpignan, there occurs an abundant deposit of organic matter, which, examined through the microscope, presented a tubular structure, in which, however, the granulations were not very distinguishable.

At Barege, one of the most powerful of the sulphureous springs, a substance is collected in the pipes and reservoirs receiving the water, which seems to consist of a cluster of little transparent irregular vesicles, having interspersed certain darkcoloured roundish bodies, that appears like the same vesicles, rendered opake by some kind of matter which fills their interior. As, however, there were signs of decomposition in this matter at the time when I was first enabled to submit it to the microscope, I considered it useless to obtain a drawing of the appearances it then presented,—and I allude to it at present, only in order to establish the general position, that the glairy or mucous-looking matter called *baregine*, which is met with in so many warm sulphureous springs, derives its origin from the growth of *Confervæ*.

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This proposition has indeed been contested by an eminent chemist at Montpellier, Professor Anglada, who is engaged in publishing an elaborate description of the thermal sulphureous waters of Roussillon *, in which he endeavours to show, that the *baregine* must be considered a chemical product, held in solution by the waters at the time they issue from the earth, and deposited by them in a flocculent form, when they come in contact with the external air.

Others, on the contrary, and amongst the rest the celebrated Vauquelin⁺, inclined to the opinion, that the substance in question had been extracted from the organic remains present in the rocks through which the mineral water found a passage, owing to the high temperature which the latter may be supposed to possess before it issues from the ground, just as gelatine is separated from bones by water under a high pressure, —a notion, unfortunately, inconsistent with the geological position of many of these springs, which proceed from granitic, or other rocks, totally destitute of all traces of organization.

It will be time, however, to discuss the probability of these chemical theories, when any specimen of the substance alluded to has been submitted to us, in no part of which signs of an organic structure can be perceived: at present it may be sufficient to remark, that since, in all the situations in which I have collected it, the greater part at least of the mass appeared to be made up of a congeries of *Confervæ* or *Oscillatoriæ*, we need not hesitate in ascribing the whole to the rapid growth of those organic bodies, to which the temperature and constitution of the thermal waters alluded to might chance to be congenial.

I am happy to be able to fortify this conclusion by the authority of Professor DeCandolle, who has assured me, that he

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formerly.

^{*} Mémoires pour servir à l'Histoire Générale des Eaux Minérales, &c.-Two volumes have already appeared. + Annales de Chimie, vol. xxviii.

formerly examined the mucous matter deposited by the waters of Valdieri in Piedmont,—a thermal spring containing sulphuretted hydrogen,—and that he fully satisfied himself, as to the whole being derived from bodies that once possessed organization, having traced the different stages of decomposition and change exhibited by the several parts of the same deposit, from a structure completely analogous to that of a *Conferva*, to a gelatinous mass in which no distinction of parts was visible.

It has been remarked, indeed, by Anglada, Gimbernat, and others who have noticed this phænomenon, that a portion of the substance in question is chemically dissolved in these waters; and although I cannot admit the proposition as a general truth, yet I have myself found, that the thermal waters of Aix in Savoy, and those of Chaudes-aigues in the department of Cantal in France, even when carefully filtered and completely transparent, begin to exhibit traces of a substance of this kind as soon as they are concentrated.

But this only proves, that the mucous matter derived from such sources is soluble in water *, and that the growth of these bodies takes place, not only in the reservoirs which receive the water after it has escaped from the earth, but also in the subterranean canals through which it finds its way in reaching the surface ;—a notion which will be admitted without difficulty, when we reflect upon the luxuriant growth of many species belonging to the lower tribes of animals and vegetables in spots equally secluded from light and the external air. Neither, if the substance called *zoogene* by Gimbernat agree in its characters with this product of the Pyrenean waters, (and I am induced to suspect that it does, from his enumerating Aix in Savoy as one of the spots in which he found it,) need we

* During the process of evaporation it seems to undergo some chemical change; for it is no longer soluble in water, when once separated from it.

be embarrassed to account for the fact he states, of his having met with it in the thermal waters of Ischia, or even in those temporary springs which are caused by the condensation of the steam disengaged from Vesuvius^{*}.

I have myself collected the water emitted from the spiracles of several volcanos, as at Ætna, Volcano, and the Solfatara of Puzzuoli; and have remarked, that it was in general perfectly pure, with the exception of a slight impregnation either of sulphuretted hydrogen, sulphureous, or muriatic acid, and that it was entirely destitute of any ingredient to which an animal or vegetable origin could be ascribed.

The deposition of *zoogene* therefore, in such situations, must be supposed, as it may be without difficulty, to have arisen from the rapid generation of certain Oscillatoria or other living bodies allied to them, owing to the temperature and chemical constitution of the water derived from this source being favourable to their existence.

To show the impossibility of supposing the organic matter to have been disengaged, according to Professor Anglada's notion, from a state of chemical solution, I may mention, that at Arles in Roussillon (the thermal water already alluded to), it occurs in great abundance, adhering in flakes to the rock, with which the hot spring comes in contact on first issuing from the earth : now this rock is inclined at so high an angle, that a substance deposited by the water could not possibly have adhered to its surface, but must inevitably have been washed down into the reservoir below, which receives the runnings from the spring, where, however; comparatively little of it is to be found.

On the other hand, it is not more difficult to account for the growth of organic bodies in such a position, favoured, as it is, by

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^{*} Bibliothèque Universelle, tom. xi. p. 410. He supposes the animal matter to be carried up along with the steam in a state of vapour.

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the genial temperature and mineral constitution of the water that flows over it, than to understand the production of Alga on the abrupt escarpment of a cliff exposed to the waves of the sea.

It would be natural to inquire, what degree of resemblance this product of warm sulphuretted springs may bear to that which Mr. Dillwyn has described, under the name of Conferva nivea*, as peculiar to the cold sulphureous waters of various parts of England and Wales. The latter was first discovered by Dr. Willan⁺ in the sulphureous water of Croft in Yorkshire, where a white hairy mucous matter is seen adhering to the sticks, grass, &c., which had been mistaken for sulphur, until Dr. Willan proved it to be of a vegetable nature, corresponding with Byssus of Linnæus[†]. He notices, as a remarkable circumstance, that this Byssus should be found below the spring no further than the water retains its sensible sulphureous qualities, as if the hepatic gas were necessary for its production and nourishment. It occurs also at Dimsdale in the same county, at Middleton-One-Row near Darlington, at Llanwrtyd in Wales,-all springs of the same quality. It grows, says Mr. Dillwyn, on roots and other substances, which it covers with white filaments two or three lines in length, and so extremely slender, that under the highest power of my microscope their thickness scarcely appeared equal to that of a horse-hair. Some of the filaments are simple, but most of them are singularly beset towards the middle with a whorl-like cluster of very simple branches, resembling proliferous shoots. Dissepiments with a high power are clearly discernible, and they divide the filaments into joints, the length and thickness of which are nearly equal.

Mr.

^{*} C. filis ramosis, tenuissimis, rigidiusculis, niveis; ramis in verticillo confertis, articulis diametrum longitudine superantibus.—*Dillwyn's Conferva*, p. 54.

⁺ Willan On Sulphureous Waters, p. 10.

[‡] I found it myself this autumn growing in great abundance at the old spring of Croft.

Mr. Dillwyn adds, in a private communication with which he has favoured me, that he has since found *Conferva nivea* abundant in the hot springs about Aix la Chapelle, especially near Frankenburg.

I leave it to the many better judges of such matters, than myself, that are to be found among the members of this Society, to pronounce, whether the body, whose appearances under the microscope are faithfully depicted in the accompanying drawing, approaches near enough to the characters of Dillwyn's Conferva nivea to be regarded as the same, or as an allied species. To this, the want of resemblance as to colour must not be regarded an objection; for the specimen I obtained at Digne, which appeared under the microscope to be the same kind of Oscillatoria as the one alluded to, was perfectly white; and M. Longchamp, in his treatise on the Waters of Vichy, informs us, that what he collected at Bareges was originally white, but became green when kept for a few days*, so that the discrepancy as to colour ought not to be looked upon as establishing a distinction of species. Neither will the difference of temperature between the sulphureous water of Harrowgate and of Greoulx be considered inconsistent with the notion of the same Conferva growing in both, when we are reminded that it has also been found by Mr. Dillwyn himself in the thermal waters of Aix la Chapelle[†].

At all events, it must be considered as a curious circumstance, that springs, of whatever temperature, which give out sulphu-

* This change also took place very rapidly in the C.nivea which I collected at Croft in Yorkshire this autumn.

+ Dr. Hooker found close to the edge of the Geysers in Iceland, and within a few inches of the boiling water, *Conferva limosa*, Dillw., a new species of *Oscillatoria*, and the finest specimens of *Jungermannia angulosa* he ever saw. In water, also, of a very great degree of heat, were, both abundant and luxurious, *Conferva flavescens* of Roth, and a new species allied to *C. rivularis*.

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retted hydrogen,—a gas so noxious to most other living bodies, should be eminently fitted to favour the growth of certain kinds of *Confervæ*, whilst thermal waters destitute of this impregnation—if I may judge from those of the Pyrenees—would seem not to deposit any organic matter of the same description.

I am aware, indeed, that similar appearances are noticed as occurring in hot springs of other kinds; but, judging from my own experience, I should be disinclined to attribute their existence, in this as in the former instance, to any peculiar property of the water. Thus, I observed on the reservoirs which received the water of the hot spring of Bagneres de Bigorre, departement des Hautes Pyrenees, a red coriaceous-looking scum covering the surface of the water, which appeared to derive its colour from a portion of oxide of iron entangled in the interstices of some kind of organic matter. It is easy to understand how it happens, that the ferruginous contents of the water, when no longer held in solution, are found to collect in this instance on the surface, and not at the bottom, of the reservoir. Every successive portion of the water, as it issues from the ground, being of a higher temperature than that which has been for some time exposed to the cooling influence of the external air, will, by virtue of its inferior specific gravity, rise to the surface, where it gives out a portion of that carbonic acid, with which it was surcharged whilst under pressure. But this gas having been the solvent of the carbonate of lime and oxide of iron which the water contained, a portion of both these ingredients will be separated at the moment of its disengagement; and, supposing any vegetable or animal matter to be at the time floating near, the earthy and ferruginous particles will be entangled within its interstices, and thereby be prevented from sinking to the bottom.

In this way I likewise account for a red scum, which I have found

found at Vichy^{*}, and in several other warm springs, that liberate carbonic acid, but are destitute of sulphuretted hydrogen^{*}, and notwithstanding the similarity of external appearance belonging to the specimens of this substance which are taken from different localities, I am inclined to doubt whether they possess anything in common, except the earthy and ferruginous matter with which they are respectively charged.

In support of this opinion, I might appeal to a drawing executed by M. Heuland, to whom I am also indebted for that of the Oscillatoria from Greoulx, which represents the appearances exhibited under the microscope by a portion of the red coriaceous-looking substance, already alluded to as having been found at Bagneres de Bigorre.

From this it would appear, that the medium, by which the earthy and ferruginous matters disengaged from the water were in that instance held together, consisted of nothing more than the *parenchyma* of decayed leaves, some of the *stomata* of which were still visible.

Without meaning indeed to deny, that *Confervæ* are met with in thermal waters of all descriptions, I am inclined to believe, that they are peculiarly abundant in sulphureous ones; for it has never occurred to me to witness, in any of the numerous mineral springs I have visited in different parts of Europe, an accumulation of organic matter at all comparable to that, which takes place in some of the sulphureous ones of the Pyrenees already alluded to; and, whereas there are many of the purer kinds of hot springs, such as that of Buxton, which do not appear to contain, or to deposit, any organic matter whatsoever, I scarcely know one containing sulphuretted hydrogen, that does not exhibit more or less of it.

* As that of Campagne in Roussillon, on the road from Carcassone to Perpignan.

XXXIII. On